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Comment on "Communication: Benzene dimer—The free energy landscape" [J. Chem. Phys. 139, 201102 (2013)]

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The benzene dimer, an important prototype system both in theoretical and experimental studies, has two competing equilibrium structures, a near T-shaped one and one in which the monomers are parallel displaced (PD). Nearly equal binding energies for these structures were found in various *ab initio* electronic structure calculations, see Ref. 1 and references therein, although a clearer preference for the T-shaped geometry emerged when it was discovered[2–4] that this structure is stabilized by a slight tilt of the monomers, giving the so-called tilted T-shaped (TT) structure. Much experimental data have been collected by various kinds of spectroscopy in the microwave, infrared, and UV regions [see Refs. 1, 5, and 6] and in all of these measurements only the (tilted) T-shaped structure was observed. In a recent Communication by Tummanapelli and Vasudevan,[7] it is argued that the exclusive observation of the T-shaped structure in experiments is due to its substantially larger stability with respect to the PD structure if one considers the free energy surface of the dimer rather than its potential energy surface. This conclusion is supported by Car-Parrinello Molecular Dynamics (CPMD) based metadynamics calculations, which yield a free energy difference between the two structures of about 21 kcal/mol at $T = 2$ K—the molecular beam temperature in the more recent experiments[5,6]—while their energies differ only by 0.2 kcal/mol. We think, however, that there are several reasons to doubt this conclusion.

The interaction between the monomers in the CPMD calculations of Ref. 7 is derived from density functional theory (DFT) calculations with the BLYP functional (Becke exchange and Lee-Yang-Parr correlation) supplemented with the empirical dispersion correction of Grimme (see Ref. 7 for references). The static energies of the dimer—relative to the free monomers—obtained from DFT calculations (although with the B3LYP functional and a different basis set, see below) are −2.5, −2.62, and −2.72 kcal/mol for the PD, T-shaped, and TT equilibrium structures, respectively (see Table S1; tables and figures labeled with S are from the supplementary material of Ref. 7). The corresponding free energy values, shown in Fig. 3 and Fig. S3, are about −6.5, −20, and −27.5 kcal/mol at $T = 2$ K. We believe that such vast differences between the energies and free energies, i.e., such large entropy effects already at $T = 2$ K, are unrealistic. One may note, for example, that the kinetic energy of free molecules at $T = 2$ K is only about 0.01 kcal/mol. Moreover, if one extrapolates the T-dependent free energies in Fig. S3 to $T = 0$ K, their differences become even larger and they deviate strongly from the static energy values mentioned above.

An additional entropy contribution may arise from the larger number (288) of equivalent TT structures, in comparison with the number (144) of equivalent PD structures. If all of these equivalent minima on the global intermolecular potential surface were accessible, this would yield an entropic stabilization of the TT structure by $k_B T \ln 2$ (where k_B is the Boltzmann constant), which is about 0.003 kcal/mol at $T = 2$ K. Some of the minima are separated by high energy barriers, however. Even if we assume that the CPMD metadynamics calculations in Ref. 7 actually access all of these structures and take into account the corresponding free energy contributions, this cannot explain the free energy difference of 21 kcal/mol, given that the energy difference is only about 0.2 kcal/mol.

An independent estimate of the size of the thermal energy and entropy contributions to the free energy can be obtained from *ab initio* electronic structure calculations, followed by (harmonic) calculations of the vibrational frequencies and rotational constants, and thus computing free energies at a given temperature from harmonic oscillator and rigid rotor expressions. Calculations of this type are described in the supplementary material.[8] They show that, indeed, the thermal energy and entropy effects at $T = 2$ K are about 0.015 kcal/mol, i.e., on the order of a few times $k_B T$.

One may question then how is it possible that the CPMD metadynamics calculations in Ref. 7 yielded such large free energy differences? We cannot answer this question, because not all of the relevant parameters of the CPMD metadynamics calculations were specified in Ref. 7 Some possible clues are given below.

The first issue that may be relevant concerns the parameters of the metadynamics treatment. In metadynamics, the free energy surface is explored by pushing the system up from its energy well(s) by adding a series of Gaussian bias potentials to the actual potential surface. The (constant) height of the bias potentials used in Ref. 7 amounts to 0.005 a.u., which is 3.14 kcal/mol. This is much larger than the energy

difference of about 0.2 kcal/mol between the TT and PD structures and the height of the energy barrier that separates these structures,[1] and even larger than the total binding energy of 2.7 kcal/mol. In the metadynamics literature,[9–11] it is recommended to use relatively high Gaussian bias potentials in the first stage of the simulation, but subsequently to lower the Gaussian heights in order to reach convergence. According to the standards in these papers, even a relatively high bias potential only amounts to a small fraction of the barrier height, however, and it is also recommended to choose Gaussians not higher than k_BT. Another important aspect is that the system should be given time to equilibrate after each energy jump and, in view of the large amount of energy added and the velocities of the molecules at $T = 2$ K, this will take many time steps.[9] In the supplementary material,[8] we show that the statistical error of the computed free energy surface increases linearly with the Gaussian height and with the update frequency. Unfortunately, the authors did not mention how many time steps were actually taken before the next bias potential was added. In Fig. 2 of their paper we noticed, however, that at $T = 2$ K, the system centers around a "tilt" angle $\theta = 66^\circ$. If the system were at equilibrium it should have equal probability to be at $\theta = 180 - 66 = 114^\circ$, but such a second maximum in the probability distribution is clearly absent from Fig. 2. Hence, we may conclude that the system was not sufficiently well equilibrated. Metadynamics MD calculations on the benzene dimer with an empirical model potential described in the supplementary material[8] confirm our suspicions.

Some further points are worth mentioning also. The "tilt" angle θ defined in Ref. 7 as the angle between the monomer planes (see Fig. S1) is not the tilt angle that was found to stabilize the tilted T-shaped structure in the *ab initio* calculations.[2–4] In the latter calculations and, in particular, in Ref. 4, the tilt of the T-shaped structure is defined differently and the monomer planes remain perpendicular. This invalidates the comparison with CCSD(T) calculations from Ref. 4 in Table S1, which is used to justify the use of DFT with the BLYP-D functional for describing the energy landscape. Furthermore, we note that the B3LYP-D method with the 311+G(2df,p) Gaussian atomic orbital basis used to compute the binding energies given in Table S1 may give rather different values than the BLYP-D method with pseudopotentials for the cores and a truncated plane wave expansion for the valence electrons that is used in the actual CPMD calculations.

In the calculations of Ref. 7, the nuclear motions were treated by a classical MD method. Quantum effects are important, however. It was found in quantum calculations of the fully coupled large amplitude (anharmonic) six-dimensional intermolecular motions[1] that the dissociation energy $D_0 = 870$ cm^{-1} $= 2.49$ kcal/mol of the (tilted) T-shaped structure is substantially smaller than the binding energy $D_e = 975$ cm^{-1} $= 2.79$ kcal/mol, because of the zero-point energy associated with the internal motions of the dimer. Moreover, it was found in this study and in Refs. 5 and 6 that quantum mechanical tunneling occurs between multiple equivalent minima in the potential surface, while these minima are separated by barriers too high to be surmounted at low kinetic energies. Such quantum effects will play an important role in the relative stability of different structures of the dimer, especially at the lowest temperature considered ($T = 2$ K).

The authors of Ref. 7 argue that the binding energy difference of 0.2 kcal/mol between the T-shaped structure and the competing PD structure is too small to explain the exclusive observation of the former. First of all, it should be mentioned that in some of the experiments only the T-shaped structure is observed, even if the PD structure were also present, because the measurement detects only polar systems. Second, it could be concluded from experiments on mixed isotopologues of the benzene dimer[12] that very small differences in binding energy—substantially smaller than the difference of 0.2 kcal/mol that is relevant here—already lead to an effective removal of the less stable species. This happens during the process of dimer formation and equilibration by collisions with rare gas atoms in the expansion region of the seeded molecular beam.

Summarizing, we think that herewith and with the additional calculations described in the supplementary material[8], we have shown that the conclusion of Ref. 7 that the T-shaped structure of the benzene dimer is strongly stabilized with respect to the competing parallel displaced structure by entropy effects is unjustified.

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